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Structural ordering tendencies in the new ferromagnetic Ni-Co-Fe-Ga-Zn Heusler alloys

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Abstract

In search for new ferromagnetic shape memory alloys (FSMA) we have calculated structural energy differences, magnetic exchange interaction constants and mixing energies of quaternary $(X_1X_2)YZ$ Heusler alloys with X_1, X_2, Y = Ni, Co, Fe and Z = Ga, Zn using density functional theory. The comparison of the energy profiles of (NiCo)FeZ, (FeNi)CoZ, and (FeCo)NiZ with Z = Ga and Zn as a function of the tetragonal distortion *c/a* reveals that the energetically preferred ordering type is (NiCo)FeGa and (NiCo)FeZn which shows that Fe prefers to occupy the same cubic sublattice as Ga or Zn what implies that Fe favors Co and Ni as nearest neighbors, respectively. The Curie temperatures of (NiCo)FeGa and (NiCo)FeZn are high of the order of 600 K. (NiCo)FeGa, which has the same valence electron concentration (e/a = 7.5) as Ni_2MnGa and also possesses a high martensitic transformation temperature (> 500 K), is of interest for future magnetic shape memory devices.

Keywords: ferromagnetic shape memory alloys; electronic properties; *ab initio* calculations;

1. Introduction

Ferromagnetic shape memory alloys may show large reversible deformations in the martensitic phase without temperature or pressure changes by simply applying an external magnetic field. The associated martensitic transformation is a diffusionless structural phase transformation from a high symmetry austenitic phase to a low symmetry martensitic phase. The intermetallic Ni_2MnGa compound is a suitable candidate, however, technological applications especially in the automotive sector of this prototype FMSA and other shape memory materials are hampered by rather low operation temperatures and brittleness. Therefore, new materials with improved properties are required.

Several candidates for future FSMAs have already been proposed, including Ni-Mn-(Al, In, Sn,Sb)[1,2], Co-Ni-(Al,Ga) [3-11] and Cu-Mn-(Al, Ga)[12,13]. We here suggest to avoid manganese as it has the tendency to form disadvantageous antiferromagnetic interactions between nearest Mn neighbors [14]. Heusler systems based on Fe,

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Co, Ni and Zn are especially interesting: The element Zn is known to be beneficial for the alloying in ternary, non-magnetic Ni- or Cu-based shape memory alloys (SMA)[15,16], but up to now Zn was not considered very often because of its high vapor pressure. Zn may substitute Sn, Al, or Ga in the X_2YZ Heusler compounds. Furthermore, FeZn alloys with a Zn concentration of 20-40% are highly magnetostrictive materials [17] similar to Fe_3Ga [18].

Recently, Ni-Fe-Ga [19-21] and Ni-Fe-Ga-Co alloys [22-24] with Co concentration between 1-9% have received attention as new FSMA. Ni-Fe-Ga is found to be more ductile than the classical Ni-Mn-based system, however its Curie temperature is below room temperature. The addition of Co strongly influences both, the martensite temperature, T_M, and the Curie temperature, T_C, and, depending on the composition, the operation temperatures are not really much enhanced. For example, substitution of Ni by Co in the $Ni_{54-x}Fe_{19}Co_xGa_{27}$ series causes an increase of T_C but decreases T_M. Whereas the replacement of Fe by Co in the $Ni_{51}Fe_{22-x}Co_xGa_{27}$ alloys increases T_C and T_M [25]. In the framework of density functional theory we have calculated the properties of quaternary, stoichiometric (NiCo)FeZ, (FeNi)CoZ, and (FeCo)NiZ Heusler alloys with Z = Ga and Zn. The structural energy differences and mixing energies are determined using the Vienna Ab initio Simulation Package (VASP) [26] while the magnetic coupling constants are obtained with the spin polarized KKR code [27]. The Curie temperatures are evaluated by inserting the calculated magnetic coupling constants into a Monte Carlo routine.

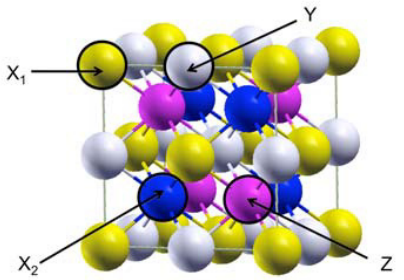

Fig.1: (color online) The cubic unit cell of quaternary $(X_1X_2)YZ$ Heusler alloys in which the transition metal atoms Fe, Co, Ni (dark blue, yellow, and light grey spheres) occupy the X_1, X_2, Y-sites while Ga (respectively Zn) occupies the Z-sites (magenta spheres).

2. Computational Details

The self-consistent calculations are carried out using VASP, a plane wave basis set and the projector augmented wave (PAW) method [26,28]. For the exchange-correlation potential the functional form of Perdew, Burke and Ernzerhof (PBE) [29,30] has been adopted. The PAW potentials include the following valence electrons: Fe: $3p^6 3d^7 4s^1$, Co: $3d^8 4s^1$, Ni: $3p^6 3d^9 4s^1$, Ga: $3d^{10} 4s^2 4p^1$ and Zn: $3d^{10} 4s^2$. All plane waves with energies below a cut-off energy of 460 eV are included in the basis set. For the integration over the Brillouin zone we have employed the tetrahedron method with Blöchel corrections and a Γ-centered 13^3 grid. For the calculation of the mixing energies we increased the number of k-points to 19^3.

In a separate calculation, we have determined the magnetic exchange coupling constants, J_{ij}, using the Munich spin polarized relativistic Korringa-Kohn-Rostoker (SPR-KKR) package, version 3.6 [27] From these J_{ij} , the Curie temperature is determined by means of Monte Carlo simulations, using a Heisenberg model and system sizes of up to 24^3 unit cells.

An easy check of phase stability is the mixing energy which is obtained by subtracting from the total energy of the alloy the sum of bulk energies of each material component *i* weightened by its concentration c_i:

$$E_{mix} = E_{alloy} - \sum_i c_i E_i \ , \qquad (1)$$

whereby negative mixing energies indicate stability against decomposition.

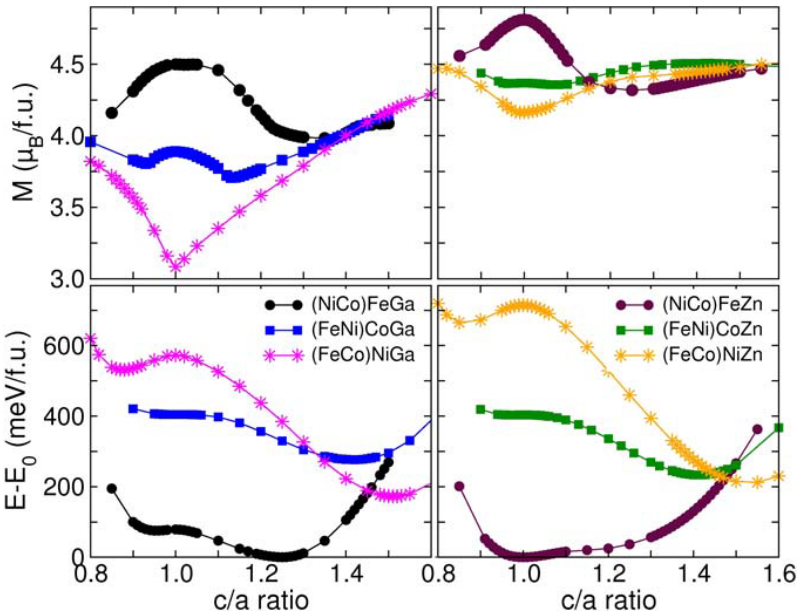

Fig.2: (color online) Total energy of (NiCo)FeZ, (FeNi)CoZ, and (FeCo)NiZ with Z = Ga (left) and Z = Zn (right) as a function of the tetragonal distortion (c/a) and the corresponding magnetic moments M in μB/f.u. All energies are relative to the energy of tetragonal (NiCo)FeZ.NiCo)FeGa and (NiCo)FeZn are energetically favored, from which follows that half of the Fe atoms preferentially share the cubic sublattice (Y-site) with Ga (or Zn) while Ni and Co occupy the X-sites (cf. Fig.1).

3. Computational Results and Discussion

When occupying all lattice sites of the quaternary $(X_1X_2)YZ$ Heusler alloy with the elements Fe, Co, or Ni (X_1, X_2, Y) and Ga or Zn (on the Z-sites) the ordering tendencies of the three transition metal elements in the neighborhood of element Z is of fundamental interest. Therefore, we have calculated the total energies at $T = 0$ K as a function of the tetragonal distortion c/a for all three different occupation possibilities which are (FeCo)NiZ, (NiCo)FeZ, and (FeNi)CoZ.

Table 1: Calculated equilibrium parameters of tetragonally distorted (NiCo)FeZ, (FeNi)CoZ, and (FeCo)NiZ with Z = Ga and Zn, respectively. Valence electron concentration, e/a, equilibrium lattice constant (for c/a = 1), a_0 , local and absolute energy minima at different c/a-ratios, magnetic moment, M and Curie temperature T_C in K for the case $c/a > 1$, energy difference between the energy minima at $c/a \leq 1$ and $c/a > 1$, $\Delta E_{c/a}$, and mixing energy. The calculation shows that the equilibrium volume of the cubic phase, $V_0 = a_0^3$, does practically not change when the system undergoes a tetragonal distortion ($c/a \neq 1$), i. e., $a^2c = a_0^3$. All energies are in meV/atom.

System	e/a	a_0 (Å)	c/a		$M(\mu_B/f.u.)$	T_C	$\Delta E_{c/a}$	E_{mix}
(NiCo)FeGa	7.5	5.757	0.95	1.25	4.04	590	19	-890
(FeNi)CoGa	7.5	5.741	1.01	1.42	4.05	365	32	-614
(FeCo)NiGa	7.5	5.716	0.88	1.51	4.19	530	90	-718
(NiCo)FeZn	7.0	5.743	1.0		4.83	733		-330
(FeNi)CoZn	7.0	5.743	0.97	1.41	4.52	600	43	-97
(FeCo)NiZn	7.0	5.741	0.85	1.55	4.52	523	28	-118

In case the material is martensitic, two energy minima exist, one at $c/a \leq 1$ and a second one at $c/a > 1$. The martensitic phase is the low-temperature phase and thus its energy should be lower than in the high temperature austenitic phase. If this condition is fulfilled a transformation from the cubic high symmetry phase (austenite) to a tetragonal phase with a lower symmetry (martensite) is possible at finite temperatures. From the energy difference between the local and the absolute energy minima we may obtain a rough guess of the martensite transformation temperature. Whether the material finally transforms martensitically depends on several factors such as the appearance of modulated structures (5M, 7M etc.) at $c/a < 1$. Further requirements for the existence of the FSM effect are high twin boundary mobility and high magnetocrystalline anisotropy energy which are not subject of this paper.

As a first step for the characterization of the new materials, we have evaluated the mixing energies (E_{mix}) which are negative for all investigated systems (cf. Table 1). This indicates that all compounds are stable with respect to segregation. In a second step the energy profiles and the corresponding magnetic moments as a function of tetragonal distortion c/a have been determined. Energetically unfavorable are the two occupation possibilities with either Fe and Co or Fe and Ni on one cubic sublattice, corresponding to (FeCo)NiZ and (FeNi)CoZ with Z = Ga or Zn (cf. Fig. 2). Lowest in energy is the ordering type (NiCo)FeGa and (NiCo)FeZn, respectively. In this case, Fe and Co, and Fe and Ni become nearest neighbors (cf. Fig. 1) which is mainly due to the excellent miscibility of Fe and Co/Ni [31]. We find the same structural ordering tendencies for both the Ga-based and the Zn-based compounds. The corresponding magnetic moments for $c/a = 1$ increase with decreasing energy of the three occupation variants, thereby stabilizing the energetically preferred structures (NiCo)FeGa and (NiCo)FeZn. For all Zn-based compounds a higher moment is found (cf. Table 1 and Fig. 2). In contrast to (NiCo)FeZn, the energy profile of (NiCo)FeGa is martensitic (cf. Fig. 2). The energy difference between the local energy minimum at $c/a < 1$ and the absolute energy minimum at $c/a > 1$ amounts to 19 meV/atom which is approximately three times larger than $E_{c/a} = 6$ meV/atom in case of Ni_2MnGa. This suggests a significantly higher martensitic transformation temperature (T_M) confirmed by free energy calculations.

The determination of the magnetic exchange coupling constants reveals strong ferromagnetic coupling for all investigated systems which is mainly dominated by the exchange interaction of nearest neighbor Fe- and Co-atoms (cf. Fig. 3). In the Zn-based compounds the coupling is found to be even stronger than in the Ga compounds giving rather high Curie temperatures up to $T_C = 733$ K for (NiCo)FeZn. We only show the magnetic coupling constants and the magnetization curves which result from the Monte Carlo simulation for the case of (NiCo)FeGa.

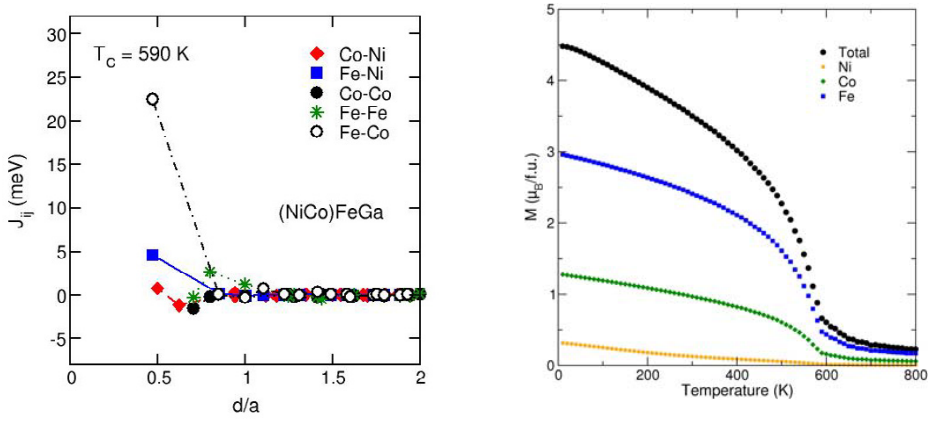

Fig. 3: (color online) Magnetic exchange coupling constants J_{ij} of $L1_0$ (NiCo)FeGa as a function of the distance d in units of the lattice constant a of the tetragonal phase (left) and variation of the individual magnetic moments as a function of temperature obtained from the corresponding Monte Carlo simulations (right). Left: The distance is measured from the respective first atom in the figure legend (cf. Fig1). Diamonds (red) mark the Co-Ni interaction, squares (blue) denote Fe-Ni, filled circles (black) describe the Co-Co, stars (green) the Fe-Fe, and open circles (black) the Fe-Co couplings. Strong ferromagnetic coupling is obtained for nearest neighbor Fe and Co spins. Right: Circles (black) mark the total moment per formula unit, squares (blue) the Fe, diamonds (green) the Co, and stars (orange) the Ni moments.

Our results indicate that in quaternary (X1X2)YZ Heusler alloys with X1, X2, Y = Ni, Co, Fe and Z = Ga, Zn, the occupation of Fe and Ga (Zn) on one cubic sublattice is energetically preferred because this maximizes the number of Fe-Co nearest neighbor pairs. Of the two favored (NiCo)FeGa and (NiCo)FeZn compounds only (NiCo)FeGa is martensitic and an estimation of the martensite temperature suggests a substantially higher value than for Ni2MnGa. The calculated Jij's allow to predict high Curie temperatures for all investigated alloys. For (NiCo)FeGa, TC amounts to 590 K.

In conclusion, our ab initio results suggest that stoichiometric (NiCo)FeGa will be a promising new FSMA. Further investigations are needed to check the existence of modulated structures for $c/a < 1$ and to determine the size of the magnetocrystalline anisotropy as well as the influence of disorder.

Acknowledgments

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